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High-field nuclear spin relaxation in liquids and solids

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Abstract. We generalise the standard theory of nuclear spin relaxation to situations in which the Markovian approximation is not applicable. Expressions for generalised frequency-dependent spin relaxation functions are presented. We show that under high-field conditions the relaxation of longitudinal magnetisation is exponential independent of the particular time dependence of the correlation functions.

1. Introduction

The modern theory of spin resonance and relaxation [1, 2] leads to a non-Markovian equation of motion for the spin-density matrix. However, explicit expressions for the relaxation functions are always given in the short-correlation-time limit: it is assumed that the relevant time correlation functions decay on a much shorter timescale than the experimental one. It is well known that this Markovian approximation does not hold in many situations of interest, e.g. in supercooled liquids and solids at low temperatures.

We therefore avoid making the Markovian approximation and present closed expressions for the generalised frequency-dependent relaxation functions.

The paper is organised as follows. In section 2 we briefly recall the derivation of the equation of motion for the spin-density matrix and the approximations implied. Following a procedure developed by Gabriel [3], we expand the density matrix into statistical tensors and calculate the relevant perturbation factors in section 3. Section 4 is devoted to the specific problems of quadrupolar and dipolar relaxation, for which analytical expressions for the frequency-dependent relaxation functions are presented in terms of Laplace transforms. Finally, we relate our results to those obtained by the Redfield theory and show that our treatment reveals an exponential decay of longitudinal magnetisation even for slowly decaying time correlation functions. Deviations from this behaviour are only to be expected for extremely short measuring times.

2. The equation of motion for the spin-density matrix

In this section we briefly recall the derivation of the equation of motion for the density matrix of a spin system coupled weakly to its surrounding (lattice) in terms of a standard projection-operator technique [4–6]. We will only consider systems of like spins.

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The Hamiltonian is of the form

$$H = H_0 + H_{\mathrm{IL}} = H_{\mathrm{I}} + H_{\mathrm{L}} + H_{\mathrm{IL}} \tag{1}$$

where H_{I}, H_{L} and H_{IL} represent the Hamiltonians of the isolated spin system, the isolated lattice and the spin–lattice interaction, respectively. H_{IL} is usually decomposed into a static and a fluctuating contribution, the former of which, averaged over lattice degrees of freedom, supplements the nuclear spin Hamiltonian:

$$\begin{aligned} H &= H_0' + \Delta H_{\mathrm{IL}} = H_{\mathrm{I}}' + H_{\mathrm{L}} + \Delta H_{\mathrm{IL}} \\ H_{\mathrm{I}}' &= H_{\mathrm{I}} + \langle H_{\mathrm{IL}} \rangle_{\mathrm{L}} \\ \Delta H_{\mathrm{IL}} &= H_{\mathrm{I}} - \langle H_{\mathrm{IL}} \rangle_{\mathrm{L}} \end{aligned} \tag{2}$$

where

$$\langle H_{\mathrm{IL}} \rangle_{\mathrm{L}} = \mathrm{Tr}_{\mathrm{L}}[\rho_{\mathrm{L}}(T) H_{\mathrm{IL}}]. \tag{3}$$

Here, $\rho_{\mathrm{L}}(T)$ denotes the lattice density matrix at a given temperature T.

In the following we shall assume that H_{I} represents the Zeeman interaction of the spin system with a constant external magnetic field $\boldsymbol{B}_0$. We did not include transverse RF fields in H_{I}, since we are interested in experiments performed by pulse techniques in this paper. Therefore, we exclude phenomena like saturation from our considerations. The more general case has been discussed e.g. by Argyres and Kelley [6].

H_{IL} (and ΔH_{IL}) is decomposed as usual in terms of irreducible tensor operators,

$$H_{\mathrm{IL}} = \sum_{KQ} (-1)^Q U_{KQ} V_{K-Q} \tag{4}$$

where U and V are spin and lattice operators, respectively.

Regarding the interpretation of H_{I}', the following remark is of importance. If one is dealing with powdered samples, the spectrum $\langle H_{\mathrm{IL}} \rangle_{\mathrm{L}}$ contains a superposition of different frequencies due to the various orientations of the relevant coupling tensors relative to the main magnetic field (in ^{2}H NMR, we observe the so-called Pake spectrum). The spin system under consideration consists of all spins which interchange energy. This means that we have to distinguish two extreme situations.

One case is represented by a system where spin diffusion is effective over the whole sample, rendering the spin system ergodic. Here, H_{I}' stands for the Hamiltonian of the whole spin system. This situation is met in most protonated systems, disregarding energy or symmetry restrictions on the spin diffusion [7].

In the other extreme, spin diffusion is only effective within one frequency line of the powder spectrum and is quenched between different ones. Thus, the spin system is not ergodic and has to be divided into subsystems of spins, which are 'on speaking terms'. Each of these subsystems is then represented by a different Hamiltonian H_{I}' according to equation (2). Consequently, all observables have to be properly averaged at the end of the calculation (see e.g. [8]).

An example of the latter behaviour is given by the heterogeneous ^{2}H spin–lattice relaxation in perdeuterated amorphous samples [9].

The Liouville–von Neumann equation for the density matrix $W(t)$ reads

$$\partial_t |W(t)) \rangle = -\mathrm{i}\boldsymbol{L} |W(t)) \rangle \tag{5}$$

where $\boldsymbol{L}$ is the Liouvillian (see appendix 2).

In order to eliminate the lattice degrees of freedom, the projection operator

$$\boldsymbol{P} = \rho_{\mathrm{L}}(T) \mathrm{Tr}_{\mathrm{L}} \tag{6}$$

is applied to equation (5) and the density matrix is decomposed into a relevant and an irrelevant part. Using standard techniques, the following equation of motion for the spin-density matrix $\sigma(t) = \mathrm{Tr}_{\mathrm{L}} W(t)$ is obtained:

$$\partial_t |\sigma(t)\rangle = -\mathrm{i}\boldsymbol{L}_{\mathrm{I}}' |\sigma(t)\rangle - \int_0^t \mathrm{d}\tau\, \underline{\boldsymbol{K}}(\tau) |\sigma(t-\tau)\rangle. \tag{7}$$

In deriving (7), the following assumptions have been made.

(i) The lattice density matrix $\rho_{\mathrm{L}}(T)$ occurring in equation (6) is independent of time and commutes with H_{L}. This ensures $[\partial_t, \boldsymbol{P}] = 0$ and is accomplished e.g. by a canonical density matrix. Consequently, equation (7) is of zeroth order in the 'back-reaction' of the spin system onto the lattice, which is a reasonable approximation because of the large heat capacity of the lattice system (for a further discussion of this point see [10]).

(ii) The initial thermodynamic state of the system is such that $\boldsymbol{P}|W(t=0)\rangle = 0$ holds. This condition is fulfilled if the lattice is initially in thermal equilibrium, a situation often encountered in NMR experiments (see, however, [1]).

In equation (7), the kernel $\underline{\boldsymbol{K}}(\tau)$ is given by

$$\underline{\boldsymbol{K}}(\tau) = \mathrm{Tr}_{\mathrm{L}}[\Delta \boldsymbol{L}_{\mathrm{IL}} \underline{\boldsymbol{S}}(\tau) \Delta \boldsymbol{L}_{\mathrm{IL}} \rho_{\mathrm{L}}(T)] \tag{8}$$

where

$$\underline{\boldsymbol{S}}(\tau) = \exp[-\mathrm{i}(1-\boldsymbol{P})\boldsymbol{L}\tau] \tag{9}$$

for time-independent $\boldsymbol{L}_{\mathrm{I}}'$.

In the following we restrict ourselves to situations where the magnetic field $\boldsymbol{B}_0$ is high enough to justify a second-order approximation with respect to the spin–lattice interaction. The relaxation kernel then reads

$$\underline{\boldsymbol{K}}_0(\tau) = \mathrm{Tr}_{\mathrm{L}}[\Delta \boldsymbol{L}_{\mathrm{IL}} \exp(-\mathrm{i}\boldsymbol{L}_0') \Delta \boldsymbol{L}_{\mathrm{IL}} \rho_{\mathrm{L}}(T)]. \tag{10}$$

Here, we consider second-rank tensor interactions only (dipole–dipole and quadrupolar interactions). (The magnetic case is completely analogous. The relevant expressions for the relaxation functions are easily obtained by generalising the expressions of [3] in a straightforward manner.)

Hence H_{IL} is written as usual [11] as

$$H_{\mathrm{IL}} = C_\lambda \sum_{\mu=-2}^{2} (-1)^\mu \boldsymbol{R}^\lambda_{2-\mu} \boldsymbol{T}^\lambda_{2\mu}. \tag{11}$$

In this expression, $\lambda = \mathrm{Q}$ means quadrupolar interaction and $\lambda = \mathrm{D}$ means dipolar interaction. The coupling constants are given by

$$C_{\mathrm{Q}} = \frac{eQ}{2I(2I-1)\hbar} \qquad C_{\mathrm{D}} = -2\gamma_{\mathrm{I}}^2 \hbar \tag{12}$$

where eQ and γ_{I} denote the quadrupolar moment and the gyromagnetic ratio of the nuclei, respectively. For further properties of the coupling Hamiltonians, see appendix 1.

The equation of motion (7) is now solved formally by means of Laplace transforms [6]:

$$|\sigma(s)\rangle = \underline{\boldsymbol{U}}(s)|\sigma(0)\rangle = [s\underline{\boldsymbol{E}} + \mathrm{i}\boldsymbol{L}_{\mathrm{I}}' + \underline{\boldsymbol{K}}_0(s)]^{-1} |\sigma(s)\rangle \tag{13}$$

which is correct up to second order in $\Delta \boldsymbol{L}_{\mathrm{IL}}$ for all times. Here, the kernel $\underline{\boldsymbol{K}}_0(s)$ is given by

$$\begin{aligned} \underline{\boldsymbol{K}}_0(s) &= \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-s\tau} \underline{\boldsymbol{K}}_0(\tau) \\ &= \frac{C_\lambda^2}{2\pi} \sum_{\mu,\mu'=-2}^{2} (-1)^\mu \int_{-\infty}^{\infty} \mathrm{d}\omega\, \hat{\boldsymbol{T}}^\lambda_{2\mu'} [(s - \mathrm{i}\omega)\underline{\boldsymbol{E}} + \mathrm{i}\boldsymbol{L}_{\mathrm{I}}']^{-1} \\ &\qquad \times [J^\lambda_{\mu,\mu'}(\omega) \hat{\boldsymbol{T}}^\lambda_{2,-\mu} + \tilde{J}^\lambda_{\mu,\mu'}(\omega) \check{\boldsymbol{T}}^\lambda_{2,-\mu}]. \end{aligned} \tag{14}$$

The meaning of the symbols $\underline{\boldsymbol{A}}$, $\hat{\boldsymbol{A}}$ and $\check{\boldsymbol{A}}$ is explained in appendix 2.

The spectral densities and time correlation are defined according to:

$$\begin{aligned} J^{\lambda}_{\mu,\mu'}(\omega) &= \int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\omega\tau} g^{\lambda}_{\mu,\mu'}(\tau) \\ \tilde{J}^{\lambda}_{\mu,\mu'}(\omega) &= \int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\omega\tau} \tilde{g}^{\lambda}_{\mu,\mu'}(\tau) \end{aligned} \tag{15}$$

and

$$\begin{aligned} g^{\lambda}_{\mu,\mu'}(\tau) &= \tfrac{1}{2}\langle [\Delta \boldsymbol{R}^{\lambda\dagger}_{2\mu'}(0), \Delta \boldsymbol{R}^{\lambda}_{2\mu}(-\tau)]_{+}\rangle_{\mathrm{L}} \\ \tilde{g}^{\lambda}_{\mu,\mu'}(\tau) &= \tfrac{1}{2}\langle [\Delta \boldsymbol{R}^{\lambda\dagger}_{2\mu'}(0), \Delta \boldsymbol{R}^{\lambda}_{2\mu}(-\tau)]_{-}\rangle_{\mathrm{L}}. \end{aligned} \tag{16}$$

Equation (14) has been derived by Gabriel [3].

The Redfield equation is obtained by applying the Markovian approximation to the equation of motion, equation (7), and using $\underline{\boldsymbol{K}}_0(\tau)$ instead of $\underline{\boldsymbol{K}}(\tau)$ therein. This is accomplished by replacing $|\sigma(t-\tau)\rangle \simeq \exp(\mathrm{i}\boldsymbol{L}'_{\mathrm{I}}\tau)|\sigma(t)\rangle$ and pushing the upper limit of the integral to infinity. The latter approximation is allowed only if the kernel $\underline{\boldsymbol{K}}_0$ has decayed to zero within the time t.

This way, one finds

$$\partial_t|\sigma(t)\rangle = -(\mathrm{i}\boldsymbol{L}'_{\mathrm{I}} + C^2_{\lambda}\underline{\boldsymbol{R}})|\sigma(t)\rangle \tag{17}$$

with

$$\underline{\boldsymbol{R}} = \int_0^{\infty} \mathrm{d}\tau\, \underline{\boldsymbol{K}}_0(\tau) \exp(\mathrm{i}\boldsymbol{L}'_{\mathrm{I}}\tau). \tag{18}$$

Here, the real and imaginary parts of $\underline{\boldsymbol{R}}$ give rise to damping (relaxation) and energy renormalisation (frequency shift), respectively.

In the next section, we shall calculate the matrix elements of equation (13) in a basis of multipole operators, representing the states of the spin system.

3. The matrix elements of the resolvent

To evaluate these matrix elements, the density operator $\sigma(s)$ is expanded into Fano's statistical tensors according to appendix 2.

From equation (13), we find, omitting the superscript λ for brevity,

$$\langle \boldsymbol{T}^{\dagger}_{kq}(s)\rangle = \sum_{k'=0}^{2I} \sum_{q'=-k'}^{k'} G^{kk'}_{qq'}(s)\langle \boldsymbol{T}^{\dagger}_{k'q'}(0)\rangle \tag{19}$$

with perturbation factors

$$G^{kk'}_{qq'}(s) = \langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{U}}(s)|\boldsymbol{T}_{k'q'}\rangle = \mathrm{Tr}_{\mathrm{I}}[\boldsymbol{T}^{\dagger}_{kq}\underline{\boldsymbol{U}}(s)\boldsymbol{T}_{k'q'}]. \tag{20}$$

Therefore, the inverse of the $(2k+1)(2k'+1)$-dimensional matrix

$$A^{kk'}_{qq'}(s) = \langle \boldsymbol{T}_{kq}|[s\underline{\boldsymbol{E}} + \mathrm{i}\boldsymbol{L}'_{\mathrm{I}} + \underline{\boldsymbol{K}}_0(s)]|\boldsymbol{T}_{k'q'}\rangle \tag{21}$$

is needed.

With the aid of the structure constants [12] defined in appendix 2, we find for the matrix elements:

$$A_{qq'}^{kk'}(s) = (s - \mathrm{i}q\omega_0)\delta_{k,k'}\delta_{q,q'} + \mathrm{i}C_\lambda \sum_{\mu=-2}^{2} (-1)^\mu \langle \boldsymbol{R}^\lambda_{2-\mu}\rangle_\mathrm{L} B^{2k'k}_{\mu q'q} + \langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{K}}_0(s)|\boldsymbol{T}_{k'q'}\rangle. \tag{22}$$

Here, the second term on the right-hand side determines the frequency spectrum. Since this is given to a very good approximation by the secular part of $\langle H_\mathrm{IL}\rangle_\mathrm{L}$ in most cases of interest [13], we will drop the terms $\mu \neq 0$ from the sum in this term in the following.

Furthermore, we have made use of

$$B^{1k'k}_{0q'q} = \left(\frac{3}{I(I+1)(2I+1)}\right)^{1/2} q\delta_{q',q}\delta_{k',k}. \tag{23}$$

The last term in (22) is evaluated according to (14) and yields

$$\langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{K}}_0(s)|\boldsymbol{T}_{k'q'}\rangle = \frac{C^2_\lambda}{2\pi} \sum_{\mu,\mu'} \sum_{K_1,Q_1} \sum_{K_2,Q_2} (-1)^\mu \int_{-\infty}^{\infty} \mathrm{d}\omega\, \langle \boldsymbol{T}_{K_1Q_1}|[(s-\mathrm{i}\omega)\underline{\boldsymbol{E}} + \mathrm{i}\boldsymbol{L}'_\mathrm{I}]^{-1}|\boldsymbol{T}_{K_2Q_2}\rangle$$
$$\times B^{2K_1k}_{\mu'Q_1q}[J_{\mu,\mu'}(\omega)B^{2k'K_2}_{-\mu q'Q_2} + \tilde{J}_{\mu,\mu'}(\omega)C^{2k'K_2}_{-\mu q'Q_2}]. \tag{24}$$

From the structure constants it is evident that the values of K_1, Q_1, K_2 and Q_2 are determined by selection rules (see appendix 2).

The spectral densities $J_{\mu,\mu'}(\omega)$ and $\tilde{J}_{\mu,\mu'}(\omega)$ are related by the fluctuation–dissipation theorem [14]. Since it can be shown [15] that the terms containing $\tilde{J}_{\mu,\mu'}(\omega)$ in (14) and (24) lead to an approach of equilibrium, we will drop them in the following. One condition necessary for doing so is the high-temperature approximation for the spin system ($|H_\mathrm{I}| \ll kT$) [15]. If in addition $|H_\mathrm{L}| \ll kT$ holds, these terms vanish by the definition of the spectral densities, equation (15). In dropping these low-temperature terms from (24), we have to replace all expectation values of the $\boldsymbol{T}_{kq}$ by the deviation from their equilibrium values; this will be done implicitly in the following.

To go on, we have to invert the matrix

$$\langle \boldsymbol{T}_{K_1Q_1}|[(s-\mathrm{i}\omega)\underline{\boldsymbol{E}}+\mathrm{i}\boldsymbol{L}'_\mathrm{I}]|\boldsymbol{T}_{K_2Q_2}\rangle = (s-\mathrm{i}\omega-\mathrm{i}Q_1\omega_0)\delta_{K_1,K_2}\delta_{Q_1,Q_2} + \mathrm{i}C_\lambda\langle \boldsymbol{R}^\lambda_{20}\rangle_\mathrm{L} B^{2K_2K_1}_{0Q_2Q_1}. \tag{25}$$

We will restrict ourselves to values $k \leqslant 2$ in the following calculations. This is not necessary, but simplifies the resulting expressions considerably. Under this condition, the last term on the right-hand side of equation (25) is given by the 'local fields':

$$Q_1\omega_\lambda := C_\lambda\langle \boldsymbol{R}^\lambda_{20}\rangle_\mathrm{L} B^{2K_2K_1}_{0Q_2Q_1} = 3Q_1\langle \boldsymbol{R}^\lambda_{20}\rangle_\mathrm{L} C_\lambda \frac{\delta_{Q_1,\pm1}\delta_{Q_1,Q_2}\delta_{K_1,K_2\pm1}}{[I(I+1)(2I+1)]^{1/2}}. \tag{26}$$

Insertion of the inverse of (25) into (24) under the restriction to axially symmetric systems [3] or random processes [16] ($J_{\mu,\mu'}(\omega) = \delta_{\mu,-\mu'}J_\mu(\omega)$) yields the following expressions for the matrix elements of the kernel $\underline{\boldsymbol{K}}_0(s)$ (dropping the low-temperature term):

$$\langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{K}}_0(s)|\boldsymbol{T}_{kq'}\rangle = \delta_{q,q'} \frac{C^2_\lambda}{2\pi} \sum_{\mu=-2}^{2} \int_{-\infty}^{\infty} \mathrm{d}\omega\, (-1)^\mu B^{2(k\pm1)k}_{\mu(q-\mu)q} B^{2k(k\pm1)}_{-\mu q(q-\mu)} J_\mu(\omega)$$
$$\times \left(\frac{s-\mathrm{i}[\omega+(q-\mu)\omega_0]}{\{s-\mathrm{i}[\omega+(q-\mu)\omega_0]\}^2+\omega^2_\lambda}\,\delta_{q,\mu\pm1} + \frac{\delta_{q,\mu}+\delta_{q,\mu\pm2}}{\{s-\mathrm{i}[\omega+(q-\mu)\omega_0]\}}\right) \tag{27}$$

and

$$\langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{K}}_0(s)|\boldsymbol{T}_{k\pm 1,q'}\rangle = \delta_{q,q'}\frac{C_\lambda^2}{2\pi}\sum_{\mu=-2}^{2}\int_{-\infty}^{\infty}\mathrm{d}\omega\,(-1)^{\mu+1}B^{2(k\pm 1)k}_{\mu(q-\mu)q}B^{2(k\pm 1)k}_{-\mu q(q-\mu)}$$
$$\times J_\mu(\omega)\frac{\mathrm{i}(q-\mu)\omega_\lambda}{\{s-\mathrm{i}[\omega+(q-\mu)\omega_0]\}^2+\omega_\lambda^2}\,\delta_{q,\mu\pm 1}. \tag{28}$$

Insertion of (27) and (28) into equation (22) for the matrix A finally gives the perturbation factors (20) via inversion.

The matrix A has a simple structure, due to the restrictions mentioned above. None of these will change the physical situation significantly.

Instead of giving expressions for the perturbation factors in the general case, we continue by considering two specific examples of spin relaxation, namely quadrupolar relaxation of spin-1 particles and dipolar relaxation.

4. Quadrupolar relaxation ($I = 1$) and dipolar relaxation

In this section we shall give explicit expressions for the frequency-dependent relaxation functions for the cases of quadrupolar relaxation of spin-1 particles and for dipolar relaxation. In the latter case our formulae will be correct only if the highest orientation of the spin system is described by statistical tensors of second rank, i.e. no octupolar order exists (for protons, this has also been called three-spin order [17]). This situation is met if we restrict ourselves to dipolar coupled pairs of spin-1/2 particles or if we assume the spin temperature concept to hold. It is easy to show [11] that in the Markovian limit the existence of a spin temperature implies $\langle \boldsymbol{T}_{3q}\rangle = \mathrm{Tr}_\mathrm{I}[\sigma(t)\boldsymbol{T}_{3q}] = 0$. We assume that the same condition is fulfilled if $\sigma(t)$ obeys the non-Markovian equation of motion, equation (7).

Of course, the formalism of the preceding sections is the same for higher orders of orientation, which occur in the case of quadrupolar relaxation of spins > 1 and for dipolar relaxation in the more general case. In this paper, however, we focus on the relaxation behaviour of observables, which obey generalised Bloch equations.

In treating quadrupolar and dipolar relaxation in the same way, one has to keep in mind the different normalisations of the corresponding coupling Hamiltonians (see appendix 1). The consequence is for $\lambda = \mathrm{D}$ that the trace operation, Tr_I, has to be normalised in order to be able to use the structure constants given in appendix 2. This implies multiplication of the corresponding expressions (equations (27) and (28)) by a factor $(\frac{1}{3})I(I+1)$, which may be absorbed in the coupling constant C_D.

Inserting the values of the structure constants for $I = 1$ into equations (27) and (28) leads to the matrix elements of the kernel $\underline{\boldsymbol{K}}_0(s)$ collected in appendix 3, equation (A3.1), with the following definition of 'local fields':

$$\begin{aligned} \lambda &= \mathrm{Q} \qquad \omega_\mathrm{Q} = \tfrac{3}{2}(e^2qQ/4\hbar)(3\cos^2\beta_\mathrm{Q} - 1 - \eta\sin^2\beta_\mathrm{Q}\cos 2\alpha_\mathrm{Q}) \\ \lambda &= \mathrm{D} \qquad \omega_\mathrm{D} = \tfrac{3}{2}\gamma_\mathrm{I}^2 r^{-3}(3\cos^2\beta_\mathrm{D} - 1). \end{aligned} \tag{29}$$

Here, the angles involved are defined in appendix 1 and r is the distance of the two spins under consideration. For $\lambda = \mathrm{D}$, we have of course to sum over all spins.

The perturbation factors are calculated according to equation (20) and are given explicitly in appendix 3, equation (A3.2). From this it is seen that only the decay of two quantum coherences is not coupled to the time evolution of any other order of coherence. All other observables do not obey generalised Bloch equations in this case, e.g. $\langle \boldsymbol{T}_{1q}(s)\rangle = G^{11}_{qq}(s)\langle \boldsymbol{T}_{1q}(0)\rangle + G^{12}_{qq}(s)\langle \boldsymbol{T}_{2q}(0)\rangle$.

Making the usual assumption of vanishing local fields ω_λ, we obtain for the perturbation factors:

$$G^{kk'}_{qq'}(s) = [s - \mathrm{i}q\omega_0 + K^k_q(s)]^{-1}\delta_{k,k'}\delta_{q,q'} \tag{30}$$

where we have used the abbreviation

$$K^k_q(s) = \langle \boldsymbol{T}_{kq}|\underline{\boldsymbol{K}}_0(s)|\boldsymbol{T}_{kq}\rangle.$$

Introducing the Hilbert–Stieltjes transform of the spectral densities as

$$J_\mu(z) = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{J_\mu(\omega)}{z - \mathrm{i}\omega} \tag{31}$$

we obtain the following expressions for the time evolution of the different orders of coherence:

$$\langle \boldsymbol{T}_{10}(s)\rangle = [s + K^1_0(s;\omega_0)]^{-1}\langle \boldsymbol{T}_{10}(0)\rangle \qquad K^1_0(s;\omega_0) = \tfrac{1}{4}C^2_\lambda \sum_{\mu=-2}^{2} \mu^2 J_\mu(s + \mathrm{i}\mu\omega_0) \tag{32}$$

$$\langle \boldsymbol{T}_{20}(s)\rangle = [s + K^2_0(s;\omega_0)]^{-1}\langle \boldsymbol{T}_{20}(0)\rangle \qquad K^2_0(s;\omega_0) = \tfrac{3}{4}C^2_\lambda \sum_{\mu=-1}^{1} \mu^2 J_\mu(s + \mathrm{i}\omega_0) \tag{33}$$

$$\begin{aligned}\langle \boldsymbol{T}_{1,\pm1}(s)\rangle &= [s_{\pm1} + K^1_{\mp1}(s;\omega_0)]^{-1}\langle \boldsymbol{T}_{1,\pm1}(0)\rangle\\ K^1_{\mp1}(s;\omega_0) &= \tfrac{1}{4}C^2_\lambda[3J_0(s_{\mp1}) + 3J_{\mp1}(s_{\mp1} \mp \mathrm{i}\omega_0)\\ &\qquad + 2J_{\pm1}(s_{\mp1} \pm \mathrm{i}\omega_0) + 2J_{\mp2}(s_{\mp1} \mp 2\mathrm{i}\omega_0)]\end{aligned} \tag{34}$$

$$\langle \boldsymbol{T}_{2,\pm1}(s)\rangle = \{s_{\pm1} + \tfrac{1}{4}C^2_\lambda[3J_0(s_{\mp1}) + J_{\mp1}(s_{\mp1} \mp \mathrm{i}\omega_0) + 2J_{\mp2}(s_{\mp1} \mp 2\mathrm{i}\omega_0)]\}^{-1}\langle \boldsymbol{T}_{2,\pm1}(0)\rangle \tag{35}$$

$$\langle \boldsymbol{T}_{2,\pm2}(s)\rangle = \{s_{\pm2} + \tfrac{1}{2}C^2_\lambda[J_{\mp1}(s_{\mp2} \mp \mathrm{i}\omega_0) + 2J_{\mp2}(s_{\mp2} \mp 2\mathrm{i}\omega_0)]\}^{-1}\langle \boldsymbol{T}_{2,\pm2}(0)\rangle \tag{36}$$

where we have introduced the new variable $s_q = s - \mathrm{i}q\omega_0$; this represents a transformation to a coordinate system rotating with angular frequency $q\omega_0$.

Equations (32)–(36) represent the essential result of the present treatment. These have the form of generalised Bloch equations. Instead of the usual relaxation rates (matrix elements of $\underline{\boldsymbol{R}}$ in equation (18)) we have generalised relaxation functions, which are Laplace transforms of memory functions. If we set s_q to zero in the arguments of the spectral densities $J_{\pm q}$, we obtain Bloch equations with the standard expressions for the relaxation rates [18]. In the case of the zero quantum coherences, $\langle \boldsymbol{T}_{k0}\rangle$, the Laplace parameter s ('inverse measuring time') appears only in combination with multiples of the Larmor precession frequency. This means that for $|\omega_0| \gg |s|$ these quantities decay exponentially in time with the decay rates defined as usual. For example, for $\lambda = \mathrm{D}$, we have in this case

$$1/T_1 = \tfrac{1}{3}\gamma^4_{\mathrm{I}}\hbar^2 I(I+1) \sum_{\mu=-2}^{2} \mu^2 J_\mu(\mathrm{i}\mu\omega_0). \tag{37}$$

(In equation (32), $K^1_0(0;\omega_0) = T_1^{-1}$.)

5. Discussion

In avoiding the Markovian approximation we have extended the range of applicability of spin relaxation theory to situations in which the correlation times are not short compared to the timescale of an NMR experiment.

The remaining restriction is determined by the second-order approximation for the spin–lattice interaction. This means that the expressions are only valid in the high-field limit.

Detailed discussions of the lineshape problem (decay of transverse magnetisation) have been given in the literature [1, 2, 19–21] and it has been pointed out that both memory effects [1, 2, 19] and higher-order corrections to the Redfield theory [20, 21] have to be taken into account in extreme physical situations. Therefore, our treatment is not applicable in the slow-motion regime in liquids.

(However, for the interpretation of FID (or solid echo) data in the motional narrowing regime, the Markovian limit of the expressions collected in appendix 3 should be used instead of equation (34) in the case of structured powder spectra, e.g. Pake spectra.)

We will focus on spin–lattice relaxation in the following discussion.

It is evident from equation (32) that our results differ from those obtained from the Redfield theory—besides the inherent statistical assumptions of that theory—by the dependence of the spectral densities upon the complex arguments $(s + i\nu\omega_0)$. Therefore, the inverse Laplace transform of (32) will only be an exponentially decaying function of time if we can neglect the dependence of $K_0^1(s;\omega_0) \equiv T_1^{-1}(s;\omega_0)$ defined in equation (32) upon s.

Let us consider first of all the simple example of an exponentially decaying time correlation function $g_\mu(t) \sim \exp(-|t|/\tau_c)$, characterised by the correlation time τ_c. In this case, we find for the spectral densities

$$J_\mu(s + i\mu\omega_0) = |\boldsymbol{R}^\lambda_{2\mu}(0)|^2[(\tau_c^{-1} + s) + i\mu\omega_0]/[(\tau_c^{-1} + s)^2 + (\mu\omega_0)^2] \qquad (38)$$

the real and imaginary parts of which give rise to damping (relaxation) and second-order energy renormalisation (frequency shift), respectively.

An expression analogous to (38) has been given by Stöckmann [22] within the framework of a statistical theory for interstitially diffusing probes in the limit of rapid diffusion.

Of course, if $\lambda = \mathrm{D}$, (38) has to be summed over the spins under consideration and τ_c has to be interpreted in an appropriate manner.

From equation (38) it is seen that J_μ becomes independent of the Laplace parameter s for times t long compared to the correlation time τ_c (or for short correlation times). This is exactly the condition necessary to push the upper limit of the integral appearing in the equation of motion, equation (7), to infinity, since τ_c characterises the decay time of the kernel $\underline{\boldsymbol{K}}(s)$. In the motional narrowing regime, this condition is fulfilled in a typical NMR experiment. However, at low temperatures, very long correlation times can be found (i.e. $\tau_c\omega_0 \gg 1$). For this situation, we again find s independent spectral densities, provided the time is long compared to the inverse Larmor precession frequency ($|s| \ll |\omega_0|$).

Another example for a time correlation function frequently found (especially in glassy systems) is the stretched exponential function $g_\mu(t) \sim \exp[-(|t|/\tau)^\beta]$, where β varies from 0 to 1 and τ is a mean correlation time. This function decays much slower to zero than the exponential one characterising a Debye process. Consequently, the Markovian approximation is not applicable even for short correlation times τ compared to τ_c in the previous example (and the definition of a narrowing condition is not straightforward). Nevertheless, if the time t is long compared to the inverse Larmor frequency, again an exponential decay of longitudinal magnetisation is observed.

The same arguments hold for more general examples of time correlation functions. The crucial point is that the inverse Larmor precession frequency determines an 'intrinsic timescale' for NMR relaxation experiments. Since ω_0^{-1} is of the order of microseconds, a non-exponential decay of longitudinal magnetisation will not be observed in a real experiment, independent of the form of the time correlation function. This also holds for time correlation functions that do not decay exponentially in a wider sense (the Kohlrausch function might be seen as a superposition of exponentially decaying functions with a mean decay time τ). Deviations from this behaviour are only to be expected for extremely short measuring times and might also be covered by experimental artefacts.

We conclude with the fact that the present treatment clearly demonstrates the applicability of conventional spin–lattice relaxation theories for a variety of physical situations not considered in detail so far.

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Appendix 1. Coupling Hamiltonians

The spin–lattice interaction reads in irreducible tensor operator notation [11]:

$$H_{\mathrm{IL}} = C_\lambda \sum_{\mu=-2}^{2} (-1)^\mu \boldsymbol{R}^\lambda_{2-\mu} \boldsymbol{T}^\lambda_{2\mu}. \tag{A1.1}$$

For $\lambda = \mathrm{Q}$ (quadrupolar interaction) and $\lambda = \mathrm{D}$ (homonuclear dipolar interaction) the coupling constants are given by

$$C_{\mathrm{Q}} = \frac{eQ}{2I(2I-1)\hbar} \qquad C_{\mathrm{D}} = -2\gamma_{\mathrm{I}}^2\hbar \tag{A1.2}$$

where eQ and γ_{I} denote the quadrupolar moment and the gyromagnetic ratio of the nuclei, respectively.

The spin operators $\boldsymbol{T}^\lambda_{2\mu}$ are normalised according to

$$\begin{aligned} &\lambda = \mathrm{Q} \qquad \mathrm{Tr}_{\mathrm{I}}(\boldsymbol{T}^{\mathrm{Q}\dagger}_{2\mu} \boldsymbol{T}^{\mathrm{Q}}_{2\mu'}) = \delta_{\mu,\mu'} \\ &\lambda = \mathrm{D} \qquad \mathrm{Tr}_{\mathrm{I}}(\boldsymbol{T}^{\mathrm{D}\dagger}_{2\mu} \boldsymbol{T}^{\mathrm{D}}_{2\mu'}) = [\tfrac{1}{3}I(I+1)]^2 \delta_{\mu,\mu'}. \end{aligned} \tag{A1.3}$$

This different normalisation may be absorbed in a different normalised trace operation. However, care has to be taken in interpreting the resulting expressions, since we have by virtue of the Wigner–Eckart theorem:

$$\begin{aligned} &\langle \boldsymbol{T}^\lambda_{1\nu} \rangle = a^\lambda_\nu \langle I_\nu \rangle \\ &a^{\mathrm{D}}_\nu = \tfrac{1}{3}I(I+1) \qquad a^{\mathrm{Q}}_\nu = \left(\frac{3}{(2I+1)(I+1)I}\right)^{1/2}. \end{aligned} \tag{A1.4}$$

These differences are not considered explicitly in the text; therefore we omit the superscript λ and write $\boldsymbol{T}_{2\mu}$ for $\lambda = \mathrm{Q}$ and for $\lambda = \mathrm{D}$.

The coupling tensors $\Delta R^{\lambda}_{2\mu}$ are given by (see equation (2)):

$$\Delta R^{\lambda}_{2\mu} = R^{\lambda}_{2\mu} - \langle R^{\lambda}_{2\mu}\rangle_{\mathrm{L}} \qquad R^{\lambda}_{2\mu} = \sum_{\nu=-2}^{2} D^{(2)}_{\nu\mu}(\Omega_{\lambda})\rho^{\lambda}_{2\nu}. \tag{A1.5}$$

Here, $D^{(2)}_{\nu\mu}(\Omega_{\lambda})$ is a Wigner rotation matrix, Ω_{λ} is the set of Eulerian angles $(\alpha_{\lambda}, \beta_{\lambda}, \gamma_{\lambda})$ required to transform the principal-axes fixed frame to the laboratory fixed frame and the $\rho^{\lambda}_{2\mu}$ denote the irreducible components of the coupling tensors in the principal-axes fixed frame, given by [11]

$$\rho^{\mathrm{Q}}_{2\mu} = \sqrt{(3/2)}\, eq\delta_{\mu,0} - (1/2)eq\eta(\delta_{\mu,2} + \delta_{\mu,-2}) \qquad \rho^{\mathrm{D}}_{2\mu} = \sqrt{(3/2)}\, r^{-3}\delta_{\mu,0} \tag{A1.6}$$

where the symbols have their usual meaning [11].

With the definition of the 'local fields' (equation (26)), the truncated Hamiltonian responsible for the spectrum reads for $I = 1$:

$$\langle H^{\lambda}_{\mathrm{IL}}\rangle_{\mathrm{L}} = \sqrt{(2/3)}\, \omega_{\lambda} T^{\lambda}_{20}. \tag{A1.7}$$

Also the Zeeman Hamiltonian may be written in terms of irreducible tensor operators:

$$H_{\mathrm{I}} = -\gamma_{\mathrm{I}} H_0 I_z = -\omega_0 I_z = -\omega_0((2I+1)(I+1)I/3)^{1/2} T_{10}. \tag{A1.8}$$

Appendix 2. Superoperators; multipole operators

We define superoperators by [23]

$$\underline{A}|B\rangle = |AB\rangle \qquad \hat{A}|B\rangle = |[A, B]_{-}\rangle \qquad \check{A}|B\rangle = |[A, B]_{+}\rangle \tag{A2.1}$$

and especially the Liouvillian:

$$L_{\kappa} := (1/\hbar)\hat{H}_{\kappa} \qquad \kappa = 0, \mathrm{I}, \mathrm{L}, \mathrm{IL}. \tag{A2.2}$$

The identity is defined by $\underline{E}|B\rangle = |B\rangle$ and the scalar product is as usual

$$\langle A|B\rangle = \mathrm{Tr}(A^{\dagger}B). \tag{A2.3}$$

Further properties of Liouville space may be found in modern textbooks on NMR [1, 2].

Expansion of the density matrix into statistical tensors [24] yields:

$$|\sigma(t)\rangle = \sum_{k=0}^{2I} \sum_{q=-k}^{k} \langle T^{\dagger}_{kq}(t)\rangle |T_{kq}\rangle \tag{A2.4}$$

with statistical tensors

$$\langle T^{\dagger}_{kq}(t)\rangle = \langle T_{kq}|\sigma(t)\rangle = \mathrm{Tr}_{\mathrm{I}}[T^{\dagger}_{kq}\sigma(t)]. \tag{A2.5}$$

The multipole operators or irreducible tensor operators obey the following normalisation and completeness relations, respectively [3]:

$$\langle T_{k'q'}|T_{kq}\rangle = \delta_{k',k}\delta_{q',q} \qquad \underline{E} = \sum_{k;q} |T_{kq}\rangle\langle T_{kq}|. \tag{A2.6}$$

For the calculation of the perturbation factors (see section 3), matrix elements of the type $\langle T_{kq}|[T_{k_1q_1}, T_{k_2q_2}]_{\pm}\rangle$ are to be evaluated. Since the (anti)commutator of two multipole operators can always be expressed in terms of multipole operators, these matrix elements just give the corresponding factors of proportionality. We follow Gabriel in denoting these matrix elements as the structure constants of the Lie algebra covered by the T_{kq}.

The values of the matrix elements are given by [12]

$$\langle \boldsymbol{T}_{kq} | \hat{\boldsymbol{T}}_{k_1 q_1} | \boldsymbol{T}_{k_2 q_2} \rangle = B^{k_1 k_2 k}_{q_1 q_2 q} \tag{A2.7}$$

with

$$B^{k_1 k_2 k}_{q_1 q_2 q} = [1 - (-1)^{k_1 + k_2 - k}](-1)^{k + 2I}(2k_1 + 1)^{1/2}(2k_2 + 1)^{1/2} \begin{Bmatrix} k_1 & k_2 & k \\ I & I & I \end{Bmatrix} \times C(k_1 k_2 k; q_1 q_2 q). \tag{A2.8}$$

Here,

$$\begin{Bmatrix} k_1 & k_2 & k \\ I & I & I \end{Bmatrix} \qquad \text{and} \qquad C(k_1 k_2 k; q_1 q_2 q)$$

denote 6*j*-symbols and Clebsch–Gordan coefficients, respectively [25]. It is evident by definition that the structure constants vanish for $k_1 + k_2 - k$ even and if the selection rules arising from the 6*j*-symbols and the Clebsch–Gordan coefficients are not fulfilled.

Some symmetry properties are given for convenience:

$$\begin{aligned} B^{k_1 k_2 k}_{q_1 q_2 q} &= (-1)^{k_1 + k_2 - k} B^{k_2 k_1 k}_{q_2 q_1 q} = (-1)^{q_1} B^{k_1 k k_2}_{-q_1 q q_2} = (-1)^{q_2} B^{k k_2 k_1}_{q -q_2 q_1} \\ &= (-1)^{k_1 + k_2 - k} B^{k_1 k_2 k}_{-q_1 -q_2 -q}. \end{aligned} \tag{A2.9}$$

The matrix elements including the anticommutator are also easily expressed in terms of slightly different structure constants:

$$\begin{aligned} \langle \boldsymbol{T}_{kq} | \check{\boldsymbol{T}}_{k_1 q_1} | \boldsymbol{T}_{k_2 q_2} \rangle = C^{k_1 k_2 k}_{q_1 q_2 q} &= [1 + (-1)^{k_1 + k_2 - k}](-1)^{k + 2I} \\ &\times (2k_1 + 1)^{1/2}(2k_2 + 1)^{1/2} \begin{Bmatrix} k_1 & k_2 & k \\ I & I & I \end{Bmatrix} C(k_1 k_2 k; q_1 q_2 q). \end{aligned} \tag{A2.10}$$

As is evident from equation (A2.10), these structure constants vanish for $k_1 + k_2 - k$ odd. For a further discussion see [3].

Using the same notation $\boldsymbol{T}_{kq}$ for $\lambda = \mathrm{Q}$ and $\lambda = \mathrm{D}$, we have to take care with respect to the meaning of I here. For $\lambda = \mathrm{Q}$, I is the spin quantum number of the nucleus, whereas for $\lambda = \mathrm{D}$ it represents the total spin of the interacting nuclei.

Appendix 3. The perturbation factors $G^{kk'}_{qq'}(s)$ for $I = 1$

Insertion of the values of the structure constants for $I = 1$ (e.g. $B^{212}_{q_1 q_2 q} = -\sqrt{3}C(212, q_1 q_2 q)$) into the expressions (27) and (28) for the matrix elements of the kernel $\underline{\boldsymbol{K}}_0(s)$ yields

$$K^{kk'}_q = \langle \boldsymbol{T}_{kq} | \underline{\boldsymbol{K}}_0(s) | \boldsymbol{T}_{k'q} \rangle$$

$$K^{11}_0(s) = \frac{1}{4\pi} C^2_\lambda \sum_{\mu=-2}^{2} \mu^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \left(\frac{s - \mathrm{i}(\omega - \mu\omega_0)}{[s - \mathrm{i}(\omega - \mu\omega_0)]^2 + \omega^2_\lambda} \delta_{\mu,\pm 1} + \frac{\delta_{\mu,\pm 2}}{s - \mathrm{i}(\omega - \mu\omega_0)} \right) J_\mu(\omega)$$

$$K_0^{12}(s) = \mathrm{i}\omega_\lambda \frac{\sqrt{3}}{4\pi} C_\lambda^2 \sum_{\mu=-1}^{1} \mu \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{J_\mu(\omega)}{[s - \mathrm{i}(\omega - \mu\omega_0)]^2 + \omega_\lambda^2} = K_0^{21}(s)$$

$$K_0^{22}(s) = \frac{3}{4\pi} C_\lambda^2 \sum_{\mu=-1}^{1} \mu^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{s - \mathrm{i}(\omega - \mu\omega_0)}{[s - \mathrm{i}(\omega - \mu\omega_0)]^2 + \omega_\lambda^2} J_\mu(\omega)$$

$$\begin{aligned} K_{\pm1}^{11}(s) = \frac{1}{4\pi} C_\lambda^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \bigg(& 3\frac{s - \mathrm{i}(\omega \pm \omega_0)}{[s - \mathrm{i}(\omega \pm \omega_0)]^2 + \omega_\lambda^2} J_0(\omega) + 3\frac{1}{s - \mathrm{i}\omega} J_{\pm1}(\omega) \\ & + 2\frac{1}{s - \mathrm{i}(\omega \pm 2\omega_0)} J_{\mp1}(\omega) + 2\frac{s - \mathrm{i}(\omega \mp \omega_0)}{[s - \mathrm{i}(\omega \mp \omega_0)]^2 + \omega_\lambda^2} J_{\pm2}(\omega)\bigg) \end{aligned} \quad \text{(A3.1)}$$

$$\begin{aligned} K_{\pm1}^{12}(s) = \mp\mathrm{i}\omega_\lambda \frac{1}{4\pi} C_\lambda^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \bigg(& \frac{3J_0(\omega)}{[s - \mathrm{i}(\omega \pm \omega_0)]^2 + \omega_\lambda^2} \\ & + \frac{2J_{\pm2}(\omega)}{[s - \mathrm{i}(\omega \mp \omega_0)]^2 + \omega_\lambda^2}\bigg) = K_{\pm1}^{21}(s) \end{aligned}$$

$$\begin{aligned} K_{\pm1}^{22}(s) = \frac{1}{4\pi} C_\lambda^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \bigg(& 3\frac{s - \mathrm{i}(\omega \pm \omega_0)}{[s - \mathrm{i}(\omega \pm \omega_0)]^2 + \omega_\lambda^2} J_0(\omega) + \frac{1}{s - \mathrm{i}\omega} J_{\pm1}(\omega) \\ & + 2\frac{s - \mathrm{i}(\omega \mp \omega_0)}{[s - \mathrm{i}(\omega \mp \omega_0)]^2 + \omega_\lambda^2} J_{\pm2}(\omega)\bigg) \end{aligned}$$

$$K_{\pm2}^{22}(s) = \frac{1}{2\pi} C_\lambda^2 \int_{-\infty}^{\infty} \mathrm{d}\omega \left(\frac{s - \mathrm{i}(\omega \pm \omega_0)}{[s - \mathrm{i}(\omega \pm \omega_0)]^2 + \omega_\lambda^2} J_{\pm1}(\omega) + \frac{2}{s - \mathrm{i}\omega} J_{\pm2}(\omega)\right).$$

From these we find for the perturbation factors via inversion of the matrix A given in equation (21) the following expressions:

$$\begin{aligned} G_{00}^{11}(s) &= X[s + K_0^{22}(s)] \\ G_{00}^{22}(s) &= X[s + K_0^{11}(s)] \\ G_{00}^{12}(s) &= G_{00}^{21}(s) = -XK_0^{21}(s) \\ X &= \{[s + K_0^{11}(s)][s + K_0^{22}(s)] - [K_0^{21}(s)]^2\}^{-1} \\ G_{\pm1,\pm1}^{11}(s) &= Y_\pm[s \mp \mathrm{i}\omega_0 + K_{\pm1}^{22}(s)] \\ G_{\pm1,\pm1}^{22}(s) &= Y_\pm[s \mp \mathrm{i}\omega_0 + K_{\pm1}^{11}(s)] \\ G_{\pm1,\pm1}^{12}(s) &= G_{\pm1,\pm1}^{21}(s) = -Y_\pm[\pm\mathrm{i}\omega_\lambda + K_{\pm1}^{21}(s)] \\ Y_\pm &= \{[s \mp \mathrm{i}\omega_0 + K_{\pm1}^{11}(s)][s \mp \mathrm{i}\omega_0 + K_{\pm1}^{22}(s)] - [\mathrm{i}\omega_\lambda + K_{\pm1}^{21}(s)]^2\}^{-1} \\ G_{\pm2,\pm2}^{22}(s) &= [s \mp 2\mathrm{i}\omega_0 + K_{\pm2}^{22}(s)]^{-1}. \end{aligned} \quad \text{(A3.2)}$$

The assumption of vanishing 'local fields' ω_λ leads to

$$\frac{s - \mathrm{i}(\omega - \mu\omega_0)}{[s - \mathrm{i}(\omega - \mu\omega_0)]^2 + \omega_\lambda^2} \simeq \frac{1}{s - \mathrm{i}(\omega - \mu\omega_0)}$$

and

$$K_q^{kk'}(s) \simeq K_q^k(s)\delta_{k'k} \qquad G_{qq}^{k'k}(s) \simeq G_{qq}^{kk}(s)\delta_{k'k}.$$

This finally yields the expressions given in section 4 in the text (equations (30)–(36)).

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